

THE SYNTHESIS OF BORON HETEROCYCLES
AS MODELS FOR
THERMALLY STABLE POLYMERS

By
GARY LEWIS STATTON

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CHAPTER I

INTRODUCTION

Criteria for Thermal Stability

The search for thermally stable polymers has been given considerable impetus in recent years due to the advances in aircraft and missile design placing more rigid requirements on the material components. It was apparent that the stability of polymers having the usual single paraffinic backbones would not suffice at high temperatures, 800-1000 degrees Fahrenheit (420-530°C), so a massive research program was initiated by government and industry to develop polymeric systems with good thermal stability in the high temperature range.

Most thermal studies up to this time had principally been on thermal reactions for syntheses or for determination of dissociation energies of bonds. Unfortunately the variance in testing conditions and the lack of any practical definition of decomposition temperature make comparisons rather difficult.

According to the Boltzman law of energy distribution among molecules, at any temperature a portion of the molecules


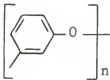
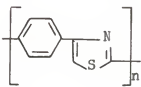
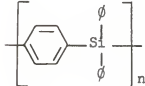
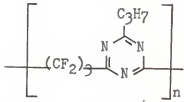
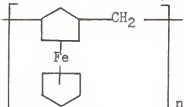
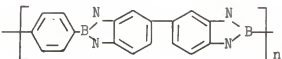
will possess energy greater than the bond energy of the weakest bond. Stability is thus not absolute but a matter of rate.¹

Although an unambiguous definition of decomposition temperatures may be given by thermodynamics or rigorous kinetics, most polymers and a large number of compounds degrade by such complex processes that the practical value of these terms is limited. The functional applications of a polymer also define temperature limitations and this point may be reached before any bond-breaking process takes place. Thus the extensive studies that have been made were based on non-rigorous kinetics and the decomposition point was assigned on an empirical basis. Also these investigations have been directed toward the thermal stability of molecules which are not polymers but compounds which could be made repeating units of a polymer. Although exact correlation between the thermal stabilities of the compound and the polymer is not always good, as may be seen in Table 1, conclusions as to the general characteristics which lead to good thermal stability can be made.

Johns^{1,2} studied the decompositions of a large number of compounds by observing isothermal pressure changes with an isoteniscope and arrived at the following conclusions:

TABLE 1

DECOMPOSITION TEMPERATURES OF A VARIETY OF COMPOUNDS AND
RELATED POLYMERS

Compound	Decomposition ² Temperature in °C. from Iso- Tenscope	Polymer	Decomposition ³ Temperature in °C. from T.G.A.
Biphenyl	543		559
Diphenyl ether	538		550
2,4-Diphenyl- thiazole	491		570
Tetraphenyl silane	482		490
2,4,6-Tris(per- fluoromethyl)- 1,3,5-triazine	482		510
Ferrocene	454		429
2-Phenyl-1,3,2- benzodiazaborole	368		553

1. All bonds in the molecule should have high dissociation energies.
2. No easy paths of decomposition should be present.
3. The structure should be stabilized by resonance.
4. Since elimination of hydrogen is one of the more common reactions of degradation, only molecules that have firmly bonded hydrogens should be used or hydrogen should be replaced by tightly bound atoms. Replacement of a carbon-hydrogen unit in benzene rings with a boron, sulfur, phosphorus or nitrogen also helps.
5. Multiple bonding can increase stability.

As a molecule is heated, the vibrational energy distributed among the bonds of the molecule increases. When the vibrational energy is equal to the dissociation energy of a bond, rupture occurs, thus the weakest bond in a complex molecule sets the maximum limit of stability. Use of the Arrhenius rate equation and known facts on alkane decomposition allows a rough calculation of 100-105 kcal./mole as the minimum dissociation energy needed to have thermal stability in a polymer at 538°C.² Table 2 shows various bond and dissociation energies commonly found in polymers. A comparison of the stability of a number of compounds of the type $(C_6H_5)_x-M$ has shown that a direct correlation exists between the bond lengths and the decomposition temperatures.⁵ A comparison of bond energies and decomposition temperatures also shows a relationship as may be seen in Table 3.

TABLE 2
DISSOCIATION AND BOND ENERGIES⁴

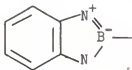
Bond	Energy Kcal./mole
C - C	82.6
C = C	145.8
$\frac{1}{2}(\text{C}-\text{C}+\text{C}=\text{C})$	114.0
C - C _{aromatic}	87.0
C - N	72.8
C = N	147.0
B - C	89.0
B - C _{aromatic}	100.0
B - O	113.0
B - N	104.0
C - H	98.7
C _{aromatic} -H	102.0
N - H	96.0

TABLE 3
 DECOMPOSITION TEMPERATURES AND BOND ENERGIES
 OF $(C_6H_5)_xM$ COMPOUNDS OF GROUP VA

Compound	Decomposition ⁵ Temperature (°C.)	Bond	Bond Energy ⁴ Kcal./mole
N,N,N'-Tetraphenyl- p-phenylenediamine	457	N-C	72.8
Triphenylphosphine	370	P-C	63.0
Triphenylarsine	307	As-C	48.0
Triphenylstibine	266	Sb-C	47.0
Triphenylbismuthine	231	Bi-C	31.0

Blake,⁵ studying the thermal decomposition of approximately one hundred organic compounds in twelve chemical classes, found that blocking the low energy decomposition paths was quite important. On the basis of bond energies alone, one would predict that N,N'-diphenyl-p-phenylenediamine would be more stable than N,N'-diphenyl-N,N'-dimethyl-p-phenylenediamine, N-H, 96 kcal./mole, versus N-CH₃, 68 kcal./mole. However the decomposition temperatures were 264°C. and 326°C., respectively. The decomposition of the N,N'-diphenyl-p-phenylenediamine proceeds by elimination of hydrogen to give N,N'-diphenyl-p-quinone-diimine. This low energy path, whose activation energy was only 28 kcal./mole as calculated by an Arrhenius plot, was prevented by substitution of the methyl groups and thus the decomposition temperature increased.

The importance of resonance can easily be seen. On the basis of similarities of spectra of benzborimidazoles to benzimidazoles, it had been expected that the aromatic system of benzborimidazoles represented by the following resonance form should result in good thermal stability.⁶



Polybenzborimidazole polymers decompose from 500-600°C.

The importance of elimination of hydrogen may be shown by the decomposition temperatures of hexafluorobenzene and pyridine, 671°C. and 621-648°C. when compared to that of benzene, 593°C.⁷

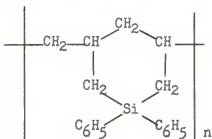
The principle of multiple bonding can increase thermal stability by two procedures. When a collision occurs at an atom which has multiple bonding, the energy of collision may be dissipated by more than one path. Also in such materials as bicyclic and cyclic compounds, bond rupture does not necessarily result in decomposition. Since the ruptured atoms are held relatively close by the remainder of the structure, the bond-breaking energy may be redistributed among the multiple bonds allowing the ruptured bond to heal.⁵ Indeed, studies on the decomposition of hydrocarbons have shown a difference in the decomposition temperatures of alkanes, cycloalkanes, and bicyclic alkanes as exemplified in Table 4.

This principle also increases the thermal stability of polymers. The cyclopolymerization of trimethylene diisocyanate was found to produce a linear cyclic polymer which was thermally stable at 150°C. higher than the corresponding linear polymer, N-ethyl-1-nylon.^{9,10} Other cyclopolymerizations of vicinal organic polyisocyanates have also substantiated their greater thermal stability.¹¹

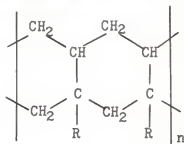
TABLE 4
DECOMPOSITION TEMPERATURES OF HYDROCARBONS⁸

Compound	Thermal Decomposition Temperature (°C.)
Cetane	373
n-Dodecane	371
n-Undecane	371
Cyclododecane	393
Bicyclohexane	396
Bicyclopentene	398
Decalin (mixed isomers)	415
Dimethyl decalin (mixed isomers)	410

Diallyldiphenylsilane, polymerized by the intra-intermolecular mechanism, has been shown to form thermally stable polymers (I) which start decomposing at 410°C.¹²



I

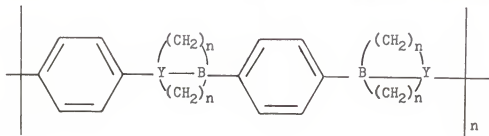


II

"Ladder" polymers (II) containing only repeating cyclic units have been obtained from polymerizing butadiene and chloroprene.¹³ These polymers decompose at 420° and 405°C., respectively.

Statement of the Problem

Polymers which would have a repeating unit consisting of alternating phenylene units and bicyclic units containing boron and another heteroatom should be expected to show some degree of thermal stability as suggested by the preceding criteria. However, the absence of information in the



literature on the preparation of aza-bora-bicyclic-alkanes or bora-phospha-bicyclic-alkanes with structures as shown in the above polymer formulation prompted an investigation of the synthesis of such model compounds. Since these laboratories have produced extensive research on unsaturated amines¹⁴⁻¹⁹ and unsaturated phosphorous compounds,^{20,21} it was felt that the bicyclic compounds could best be synthesized by the hydroboration of the unsaturated amines and phosphines by phenylborane or through the use of an amine complex of phenylborane. A report of the preparation of a stable tricyclic compound from trimethylamine-borane and triallylamine also stimulated interest in this procedure.²²

Several difunctional intermediates which would lead to polymers also were to be synthesized so that polymers could be made if the model compounds proved obtainable.

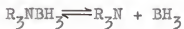
Historical Notes on Amine-boranes as Hydroborating Agent

The first literature reference to a borane reacting with an amine was submitted by Frankland²³ in 1862. Since then, the interest in boron compounds and boranes coordinated with nitrogen in amines has resulted in a countless number of papers on their syntheses. It has only been recently that their use as synthetic tools for the organic and inorganic chemist has been realized.

Köster²⁴ reported the synthesis of perhydro-9-b-boraphalene from the hydroboration of cyclododeca-1,5,9-triene with triethylamine-borane in 1957.

Hawthorne²⁵ found that pyridine-borane would react with terminal olefins using diglyme as solvent at temperatures of 100°C. It was suggested that the amine-borane decomposed to the borane at the elevated temperatures and borane then reacted with the olefin.

The reactions of various trialkylamine-boranes with olefins to form trialkylboranes in 78-95 per cent yields were reported by Ashley.²⁶ The reactions were run without solvents. Ashley also concluded that the trialkylamine-boranes decomposed at elevated temperatures.

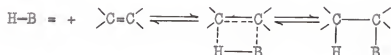


Köster^{27,28} found that the reactions of trialkylamine-boranes with diolefins provided a convenient route to cyclic boranes. Hawthorne^{29,30} then proceeded a step further by reacting trimethylamine-t-butylborane with a number of olefins and diolefins. Two of the olefins, divinyl ether and divinyl silane, provided the first example of preparation of heterocyclic compounds containing boron and another element by this method.

Adams and Poholsky³¹ recently prepared the first 1,2-aza-boro-cycloalkane by refluxing a toluene solution of

N,N'-dimethyl-allylamine with trimethylamine-borane. A report on the preparations of 1-methyl-2-phenyl-1,2-azaborolidine and 2-phenyl-1,2-azaboracyclohexane from the reactions of N-methylallylamine and 3-butenylamine with trimethylamine-phenylborane in diglyme soon followed.³²

The mechanism of the reaction of amine-boranes with olefins has been concluded to require that the amine-borane reagent dissociates by an equilibrium reaction as stated above. The monomeric borane then reacts with the olefin. Brown^{33,34} has suggested that this reaction occurs by a four-center cis addition.



Source and Purification of Materials

n-Propyl bromide, sec-butyldiallylamine and lithium aluminum hydride were obtained from Penninsular Chem Research, Incorporated. The n-propyl bromide and sec-butyldiallylamine were distilled before use.

p-Dibromobenzene was obtained from Distillation Products Industries, Division of Eastman Kodak Company and was used as received.

Diallylamine and allylamine were obtained from the Shell Chemical Corporation and were distilled before use.

p-Phenylenediamine was obtained from Fischer Scientific Company and was used without further purification.

Trimethylborate was obtained from Callery Chemical Company and was used as received.

N,N-Diallylaniline, N-allylaniline, N,N'-diallylpiperazine and N-allylpiperidine were prepared by former students of Dr. George B. Butler and were distilled before use.

4-Bromo-1-butene was prepared by W. C. Bond and was 97 per cent pure as determined by gas-liquid chromatographic analysis.

Equipment and Treatment of Data

Temperatures recorded in this paper are uncorrected and are in degrees centigrade.

Infrared data were obtained with a Perkin-Elmer Infracord Double-beam Infrared Recording Spectrophotometer.

Nuclear magnetic resonance data were obtained with a Varian DP-60 High Resolution Nuclear Magnetic Resonance Spectrometer.

Mass spectral data were obtained on a Bendix Time of Flight Mass Spectrometer.

Several molecular weights were obtained on a Mechrolab 302 Vapor Pressure Osmometer.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee or Schwarzkopf Micro-analytical Laboratory, Woodside, New York.

CHAPTER II

PREPARATION OF UNSATURATED SECONDARY AND TERTIARY AMINES

General Discussion

Not all of the unsaturated secondary and tertiary amines were available commercially, thus it was necessary to prepare several of them as intermediates. The amines were prepared either by the method of Butler and Bunch¹⁴ or the classical method of Hofmann.³⁵

The former involves the addition of the alkenyl halide to a slurry of sodium carbonate and the primary or secondary amine in water. The reactions were carried out in a three-necked, round-bottom flask fitted with a mechanical stirrer, a cold-water reflux condenser and an addition funnel. The reaction mixtures were heated to approximately 100° by means of a Glass-Col heating mantle and were maintained at this temperature during the entire reaction period of 24 to 72 hours. The contents of the flasks were filtered when cool. The amine layers were separated and dried over a suitable drying agent. All amines except N,N,N',N'-tetraallyl-p-phenylenediamine were purified by fractional distillation through a 1.5 x 23 cm.

column packed with stainless steel protruded packing and insulated by an outer glass jacket. N,N,N',N'-Tetraallyl-p-phenylenediamine was purified through preparation of the hydrochloride salt. The salt was then reacted with base and the amine distilled in a Hickman molecular still at pressures of 10^{-3} to 10^{-4} mm.

The other method for preparation of amines involved reaction of base with the ammonium salt formed from the alkyl halide and the appropriate primary or secondary amine. The reactions were carried out in a one-neck, round-bottom flask equipped with a cold-water condenser. The amines were then purified by fractional distillation as in the other procedure.

Several of the tertiary amines prepared have not previously been reported in the literature and picrate derivatives of these amines were prepared by the standard procedure.³⁶ A sample of the amine was added to a small quantity of 95 per cent ethanol and this was added to an equal quantity of a saturated solution of picric acid in 95 per cent ethanol. The solution was heated to boiling, allowed to cool slowly and the yellow crystals of picrate were filtered and recrystallized from ethanol.

Experimental

Synthesis of diallylethylamine.--Diallylamine

(97.2 g., 1.0 mole) and 109.0 g. (1.0 mole) of ethyl bromide were placed in a 500 ml. flask. The solution was allowed to stand overnight whereupon a white crystalline solid formed. After adding 84.0 g. (1.5 mole) of potassium hydroxide pellets to the solid, the mixture was shaken occasionally during which time heat was evolved. After ten hours, the mixture was filtered and the amine was fractionally distilled at atmospheric pressure yielding 73.3 g. (58%) of a clear colorless liquid, b.p. 128-130°, n_D^{20} 1.4371, lit.³⁷ b.p. 129-130°, n_D^{20} 1.4360.

Synthesis of diallyl-n-propylamine.--To a 500 ml.

flask were added 126.0 g. (1.3 mole) of diallylamine and 123.0 g. (1.0 mole) of n-propyl bromide. The reagents were allowed to set overnight during which time a crystalline solid formed. After 60.0 g. (1.5 mole) of potassium hydroxide pellets was added, the mixture was shaken occasionally and allowed to set for a period of two days. The mixture was filtered and the amine was fractionally distilled at atmospheric pressure yielding 92 g. (65%) of a clear colorless liquid, b.p. 150-151°, n_D^{21} 1.4354; picrate, m.p. 86-88°.

Anal. Calcd. for $C_9H_{17}N$: C, 77.64; H, 12.31; N, 10.06. Found: C, 77.41; H, 12.11; N, 10.24.

Synthesis of allyl-n-propylamine.--The Hofmann procedure was used to synthesize this amine. The reagents, 61.5 g. (.50 mole) of n-propyl bromide and 28.5 g. (.50 mole) of allylamine, were placed in a 200 ml. flask. After stirring the solution by shaking, an exothermic reaction occurred and the appearance of small amounts of a white solid were noted. The mixture was allowed to set overnight, then 39 g. (.7 mole) of solid potassium hydroxide pellets was added. The mixture reacted immediately forming a flaky white solid and a yellow liquid. The mixture was filtered and the liquid fractionally distilled yielding 23.5 g. (47%) of a clear colorless liquid, b.p. 109-110°, lit.³⁸ b.p. 110-114°.

Synthesis of allyl-3-butenyl-n-propylamine.--This synthesis was carried out using the procedure of Butler and Bunch.¹⁴ To vigorously stirring slurry of 10.6 g. (.10 mole) of sodium carbonate, 30 ml. of water and 11 g. (.11 mole) of allyl-n-propylamine, 17.4 g. (.13 mole) of 4-bromo-1-butene was added dropwise. The mixture, kept at approximately 100°, was stirred for 24 hours, cooled, then filtered. The amine layer was separated, dried over sodium hydroxide and fractionally distilled yielding 10.6 g. (66%) of a

clear colorless liquid, b.p. 79-80° (33 mm.), n_D^{21} 1.4409; picrate, m.p. 77-78.5°.

Anal. Calcd. for $C_{10}H_{19}N$: C, 78.36; H, 12.50; N, 9.14. Found: C, 78.78; H, 12.63; N, 9.33.

Synthesis of di(3-butenyl)-n-propylamine.--The procedure for preparation of this compound was essentially that of Butler and Bunch.¹⁴ The 4-bromo-1-butene (60.5 g., .45 mole) was added dropwise to a slurry of 32 g. (.30 mole) of sodium carbonate, 60 ml. of water and 13 g. (.22 mole) of n-propylamine. The heated mixture was allowed to stir for 24 hours. The mixture on cooling was filtered. The amine layer was separated, dried over sodium hydroxide pellets and distilled yielding 19.8 g. (51%) of a clear colorless liquid, b.p. 93-94° (30 mm.), n_D^{22} 1.4442; picrate, m.p. 104-106°.

Anal. Calcd. for $C_{11}H_{21}N$: C, 78.96; H, 12.65; N, 8.37. Found: C, 78.89; H, 12.78; N, 8.52.

Synthesis of N,N-di(3-butenyl)aniline.--The procedure used for preparation was essentially that of Butler and Bunch.¹⁴ The 4-bromo-1-butene (60.5 g., .45 mole) was added dropwise to a stirring slurry of 32 g. (.30 mole) of sodium carbonate, 50 ml. of water and 20.5 g. (.22 mole) of aniline. The mixture was stirred and heated for 72 hours, allowed to cool, then filtered. The amine layer was separated, dried

over sodium hydroxide pellets and distilled yielding 18.3 g. (41%) of a clear colorless liquid, b.p. 91-93° (.6 mm.), n_D^{23} 1.5419.

Anal. Calcd. for $C_{14}H_{19}N$: C, 83.54; H, 9.51; N, 6.96. Found: C, 83.38; H, 9.66; N, 6.93.

Synthesis of N,N,N',N'-tetraallyl-p-phenylene-diamine.--The procedure for preparation of this compound was that of Butler and Bunch¹⁴ with some modifications. A water solution of 106 g. (1.0 mole) of sodium carbonate, 19.4 g. (.18 mole) of p-phenylenediamine and 96.8 g. (.80 mole) of allyl bromide was added to a 500 ml. flask. The mixture was allowed to react for 72 hours, whereupon a tarry black liquid layer formed. This layer was extracted with benzene, separated and dried. Gaseous hydrochloric acid was passed into the benzene solution resulting in the precipitation of 16 g. of solid which was washed with acetone. The white solid decomposed at 204-205°. This ammonium salt was then slowly added to a water solution of sodium carbonate. This solution was extracted with ether. The ether solution was dried over sodium hydroxide and placed on a flash evaporator where the ether was removed. The remaining liquid was then distilled in a commercial Hickman still yielding 11.6 g. (22%) of a pale yellow liquid, n_D^{25} 1.5637. A small portion of the pale yellow amine was

redistilled through a micro 10 cm. Vigreux column giving the boiling point as 133-134° (.08 mm.). There was no change in the refractive index or color of the distillate. Picrate, m.p. 140-142° (dec.).

Anal. Calcd. for $C_{18}H_{24}N_2$: C, 80.54; H, 9.01; N, 10.44. Found: C, 80.33; H, 8.95; N, 10.59.

CHAPTER III

PREPARATION OF AN UNSATURATED PHOSPHINE

Experimental

Synthesis of diallylphenylphosphine.--The procedure used to prepare the phosphine was a modification of the method of Jones.³⁹ Since the final product is easily oxidized in air, all transfers and reactions were carried out under a nitrogen atmosphere. The Grignard reagent was prepared by addition of 96.7 g. (.80 mole) of allyl bromide to a mixture of 300 ml. of ether and 19.2 g. (80 g. atom) of magnesium in a one-liter, four-neck, round-bottom flask fitted with a cold-water condenser, an addition funnel, a low temperature thermometer, and a mechanical stirrer. A nitrogen inlet tube was attached to the condenser. After the initial start of the reaction, the flask and contents were cooled in an ice bath. The addition of the halide was adjusted so the temperature would remain below 10°. After complete addition of the allyl bromide, the stirring mixture was allowed to warm to room temperature. The contents of the flask were cooled to -70° with a dry ice-acetone bath and an ethereal solution containing 59.5 g. (.33 mole) of

dichlorophenylphosphine was added dropwise. The mixture was allowed to warm to room temperature overnight. It was hydrolyzed with a 20 per cent water solution of ammonium chloride resulting in two layers. The ether layer was separated, dried and fractionally distilled through a 30 cm. vacuum jacketed Vigreux column yielding 29.5 g. (48.7%) of a clear colorless liquid, b.p. 84-85° (1.1 mm.), lit.³⁹ b.p. 127° (14 mm.).

CHAPTER IV

PREPARATION OF BORON INTERMEDIATES

General Discussion

The boron intermediates were prepared by procedures reported in the literature with some modification. Phenylboronic acid was prepared from trimethyl borate and phenylmagnesium bromide using the procedure described by Washburn and co-workers.⁴⁰ The phenylboronic acid was converted to the diethyl ester by azeotropic distillation.^{41,42} The diethyl phenylboronate was then reduced by lithium aluminum hydride in the presence of triethylamine to give triethylamine-phenylborane.⁴²

Phenylenediboronic acid was prepared by the method of Nielsen and McEwen⁴³ from the Grignard reagent of p-dibromobenzene and trimethyl borate. The previously unreported tetraethyl ester was then prepared by the same procedure as diethyl phenylboronate. The attempt to reduce the tetraethyl-p-phenylenediboronate with lithium aluminum hydride failed. The reaction was run in diethyl ether and at the temperature used, the ester and the lithium aluminum hydride co-precipitated. Possibly the use of a different

solvent would correct the problem. All apparatus used in these reactions were purged with nitrogen for several hours before use.

Experimental

Synthesis of phenylboronic acid.--Phenylmagnesium bromide was prepared by the dropwise addition of 157.0 g. (1.0 mole) of bromobenzene in ether to a mixture of ethyl ether and 36.0 g. (1.5 g. atom) of magnesium in a one-liter, four-neck, round-bottom flask equipped with a thermometer, mechanical stirrer, addition funnel and a cold-water condenser. After the reaction was initiated, the contents of the flask were cooled to 10° with an icebath. Upon complete addition of the halide, the mixture was allowed to warm to room temperature. Trimethyl borate (103.9 g., 1.0 mole) and 800 ml. of ether were placed in a two-liter, three-neck, round-bottom flask equipped with a mechanical stirrer, a low temperature thermometer and by means of a Claisen adapter, a nitrogen inlet tube and an addition funnel. The solution was cooled with a dry ice-acetone bath and the Grignard reagent was added at a rate which kept the reaction mixture at -65 to -70°. During the addition, the reaction mixture was vigorously stirred. After complete addition, the mixture was allowed to warm to room temperature overnight and then hydrolyzed with 10 per cent sulfuric acid. The

ether layer was separated and placed in a two-liter, three-neck, round-bottom flask fitted with an addition funnel, mechanical stirrer and a Claisen distilling head. As the ether solution was concentrated, 1.0 liter of water was added slowly until the temperature at the distilling head reached 98°. The solution was then cooled whereupon a solid precipitated. The mixture was filtered and the solid was washed with hexane and dried, yielding 105 g. (90%) of white solid, m.p. 212-215°, lit.⁴⁰ m.p. 215-216°.

Synthesis of diethyl phenylboronate.---Phenylboronic acid (50.0 g., .41 mole), 320 g. (4.0 mole) of benzene and 138 g. (3.0 mole) of absolute ethyl alcohol were placed in a two-liter, one-neck, round-bottom flask. The flask was connected to a azeotropic distillation setup consisting of a packed distillation column, a Dean-Starke trap, a cold-water condenser and a drying tube. A thermometer was hung inside the condenser so that the mercury bulb was slightly above the overflow in the Dean-Starke trap. The contents of the flask were heated by a Glass-Col mantle and a ternary azeotrope of benzene, alcohol and water distilled over at 64° forming two layers in the trap. The lower layer was continuously removed. After seven days of continuous distillation, the temperature rose to 68° where the binary alcohol and benzene azeotrope distilled. The trap and condenser

were then replaced by a distilling head and the remaining alcohol and benzene removed. The remaining liquid was distilled under reduced pressure giving 69 g. (92%) of a clear colorless liquid, b.p. 52-55° (.5 mm.), lit.⁴⁴ b.p. 50° (.4 mm.).

Synthesis of triethylamine-phenylborane.--Lithium aluminum hydride (6.9 g., .18 mole) was added to 600 ml. of dried diethyl ether in a one-liter, four-neck, round-bottom flask fitted with a condenser with a nitrogen inlet tube, a mechanical stirrer, an addition funnel and a low temperature thermometer. The mixture was refluxed for thirty minutes, then cooled to -72° with a dry ice-acetone bath. After 32.9 g. (.325 mole) of triethylamine was added to the stirring mixture, an equal molar quantity of diethyl phenylboronate was added dropwise. After complete addition, the mixture was stirred for another hour at -72° then allowed to warm to room temperature. The mixture was then filtered and the filtrate cooled in a dry ice-acetone bath resulting in precipitation of a solid. The solid was filtered off and recrystallized from ether in a similar manner yielding 40 g. (65%) of a white crystalline solid, m.p. 63-65°, lit.⁴² m.p. 64-65°.

Synthesis of p-phenylenediboronic acid.--A solution of tetrahydrofuran and 47.0 g. (.20 mole) of p-dibromobenzene

was added dropwise to a stirring mixture of 11 g. (.45 g. atom) of magnesium and 100 ml. of tetrahydrofuran in a 500 ml., three-neck, round-bottom flask equipped with an addition funnel, stirrer and a cold-water condenser. After complete addition, the mixture was refluxed for six hours. A solution of 300 ml. of diethyl ether and 51.5 g. (.5 mole) of trimethyl borate in a one-liter, four-neck, round-bottom flask, equipped with a mechanical stirrer, a low temperature thermometer, an addition funnel and a nitrogen inlet tube, was cooled to -72° . The Grignard reagent was added rapidly, keeping the temperature at -70° . After complete addition, the mixture of a white solid and ether solution was stirred at -70° for thirty minutes and then allowed to warm to room temperature. The mixture was hydrolyzed with dilute hydrochloric acid until two layers remained. The organic layer was separated and dried with anhydrous magnesium sulfate. The ethers were removed on a flash evaporator leaving a solid which was washed thoroughly with ether, filtered, washed with water and filtered again. The dry white solid (26.2 g.) did not melt at up to 250° .⁴³

Synthesis of tetraethyl-p-phenyldiboronate.--The 26.2 g. of solid containing p-phenylenediboronic acid, 160 ml. of dry benzene and 200 ml. of absolute ethyl alcohol were mixed in a 500 ml., round-bottom flask. The

flask was connected to the azeotropic distillation setup described above and treated in a similar manner. The final fractional distillation yielded 18.1 g. of a clear colorless liquid, b.p. 128° (1.6 mm.), which hydrolyzed on exposure to moist air. The overall yield was 31 per cent based on the p-dibromobenzene.

Anal. Calcd. for $C_{14}H_{24}B_2O_4$: C, 60.49; H, 8.70; B, 7.78. Found: C, 60.26; H, 8.45; B, 7.65.

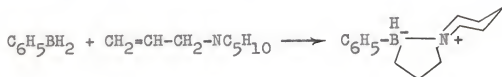
Attempt to prepare di(triethylamine)-p-phenylene-diborane.--Lithium aluminum hydride (3.8 g., .10 mole) was refluxed with 150 ml. of diethyl ether for thirty minutes in a 300 ml., three-neck, round-bottom flask fitted with a cold-water condenser, a mechanical stirrer and an addition funnel. The mixture was cooled to -72° with a dry ice-acetone bath and 14.0 g. (.13 mole) of triethylamine was added. The tetraethyl-p-phenylenediboronate (18.1 g., .065 mole) was added dropwise and small lumps of grey material formed. The mixture was stirred for thirty minutes after complete addition and then allowed to warm to room temperature. The contents of the flask were filtered and the filtrate concentrated by removal of ether. The solution was cooled to -72° but no precipitate resulted and no evidence of the desired product could be found.

CHAPTER V

PREPARATION OF BORON HETEROCYCLES

General Discussion and Results

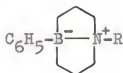
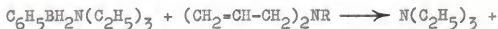
The syntheses were first attempted by reduction of diethyl phenylboronate with lithium aluminum hydride in the presence of the unsaturated amine at low temperatures. The reaction mixture was then distilled and isolation of products was attempted by crystallization at low temperatures or distillation. N,N-diallylaniline was used in these attempts since the bicyclic product from this compound should be the best model of the proposed polymer. These reactions did not lead to the stable compounds which had been expected and the easily oxidized products could not be identified. In order to determine if this procedure was resulting in the hydroboration of the double bond, a less complex amine, N-allylpiperidine, was used since the number and complexity of the products would be lessened. The amine was treated in similar fashion and a small amount of the product (13%) was isolated.



The product, 1-phenyl-1-bora-5-azoniaspiro [4.5] decane was stable in the atmosphere. The presence of the nitrogen to boron link could be seen by the shift of the boron-hydrogen stretching frequency to 4.3 microns which is indicative of co-ordination compounds of boranes.⁴⁵

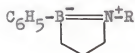
Similar reactions were then run on diallylethylamine and diallyl-n-propylamine. The only products which could be isolated were small amounts of clear colorless liquids which readily oxidized in air. These liquids were later proved to be substituted 1,2-azaborolidines. Since this procedure did not appear to give the desired product, the syntheses were attempted by the use of triethylamine-phenylborane and the unsaturated amines. These reactions were performed by heating dilute toluene solutions of the reagents and slowly distilling the solutions. Two isolatable products resulted from these reactions, clear colorless liquids and white solids. Apparent polymeric viscous liquids were also formed but were not investigated. The clear colorless liquids oxidized easily in air, turning brown after a short period of time. The white solids were

stable in air and were proved to be bicyclic compounds having structure I.



I

+



II

The liquids were assigned structure II and were the main isolatable products. Table 5 shows the product and yield obtained from the appropriate amine.

The structure assignments were made on the basis of n.m.r. spectra, infrared spectra and analyses. Mass spectral data and molecular weights were also obtained for several compounds.

Mass spectral data were obtained for two of the liquids. The spectra of 1-n-propyl-2-phenyl-1,2-azaborolidine showed a parent ion peak at 187 mass units which agrees with the calculated molecular weight of 187.08. The most intense peak was found at 158 mass units and small absorptions were recorded at 116 and 89 mass units. The loss of an ethyl group gives the peak at 158 mass units. This is consistent with the most probable mode of rupture of amine compounds.⁴⁶ The two weak peaks are the result of

TABLE 5
 PRODUCTS AND YIELDS OF THE REACTION OF TRIETHYLAMINE-PHENYLBORANE AND TERTIARY
 DIALLYLAMINES

Diallylamine Reagent			Products and Yields
Diallylethylamine	1-Ethyl-2-phenyl- 1,2-azaborolidine	22%	1-Ethyl-5-phenyl-1-aza-5- borabicyclo [3.3.0] octane 7.0%
Diallylpropylamine	1-n-Propyl-2-phenyl- 1,2-azaborolidine	31%	1-n-Propyl-5-phenyl-1-aza- 5-borabicyclo [3.3.0]- octane 8.0%
sec-Butyldiallylamine	1-sec-Butyl-2-phenyl- 1,2-azaborolidine	21%	1-sec-Butyl-5-phenyl-1- aza-5-borabicyclo [3.3.0]- octane 9.5%
N,N-diallylaniline	1,2-Diphenyl- 1,2-azaborolidine	30%	1,5-Diphenyl-1-aza-5- borabicyclo [3.3.0] octane 22.0%

loss of the $C_3H_7N-CH_2-$ and $C_3H_7N-C_3H_6-$ groups. The spectrum of 1-sec-butyl-2-phenyl-1,2-azaborolidine showed a parent ion peak at 201 in agreement with the calculated molecular weight of 201.11. The most intense peak in the spectrum was at 172 mass units corresponding to loss of the ethyl group beta to the nitrogen atom. Three other peaks of weaker intensity were found at 186, 130 and 89 mass units. These may be rationalized by considering the loss of $-CH_3$, C_4H_9N- and $C_4H_9N-C_3H_6-$ groups. The relative intensities of the peaks also are indicative of the structure assignment. The spectra showed that all peaks resulting from fragmentation in which two bonds were broken were less intense than the parent ion peak.

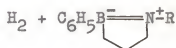
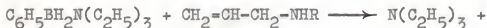
The infrared spectra of the liquids were in agreement with the assigned structures. It has been reported that boron-nitrogen bonds in aminoboranes absorb in the region of 6.6 to 7.3 microns.^{32,47,48} Table 6 shows the boron-nitrogen absorptions of the 1,2-azaborolidines prepared by this research. The absorptions were easily confirmed by partial hydrolysis of the substituted 1,2-azaborolidines which breaks the boron-nitrogen bond and results in a decrease in intensity of the boron-nitrogen absorption. The infrared spectra also showed the absence of boron-hydrogen and olefinic bonds.

TABLE 6
INFRARED ABSORPTION OF THE B-N BOND IN SUBSTITUTED
1,2-AZABOROLIDINES

Compound	B-N Absorption Band in Cm^{-1} and Microns	
1-Ethyl-2-phenyl-1,2-azaborolidine	1512	(6.63)
1-n-Propyl-2-phenyl-1,2-azaborolidine	1504	(6.65)
1-sec-Butyl-2-phenyl-1,2-azaborolidine	1504	(6.65)
1,2-Diphenyl-1,2-azaborolidine	1389	(7.20)

Nuclear magnetic resonance spectra were obtained on several of the 1,2-azaborolidines. The boron resonance was obtained for 1-ethyl-2-phenyl-1,2-azaborolidine and was found at -23 ppm. relative to trimethylborate. The proton magnetic resonance spectral data for three of the 1,2-azaborolidines are given in Table 7. The spectra were obtained on the neat liquids using acetaldehyde as the external standard.

Two 1,2-azaborolidines were also prepared by the reaction of secondary allylamines and triethylamine-phenylborane. Thus the reaction of triethylamine-phenylborane with N-allylaniline resulted in isolation of 1,2-diphenyl-1,2-azaborolidine. Use of allyl-n-propylamine resulted in 1-n-



propyl-2-phenyl-1,2-azaborolidine. The infrared spectra of the compounds prepared in this manner were identical with those from the tertiary diallylamines.

The proton magnetic resonance spectral peaks for several of the 1-aza-5-borabicyclo [3.3.0] octanes are given in Table 8. The spectra were obtained on the solids dissolved in carbon tetrachloride using acetaldehyde as the external standard. The hydrogen absorptions of the first

TABLE 7

N.M.R. SPECTRAL DATA OF SUBSTITUTED 1,2-AZABOROLIDINES

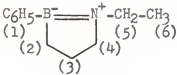
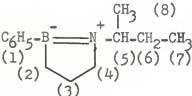
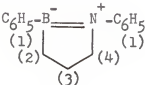
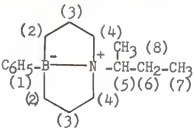
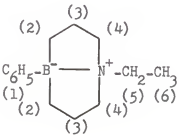
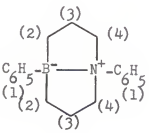
Compound	Peak Assignment	τ	Areas
	1	3.33	5.0
	4,5	7.41	4.0
	3	8.79	
	2	9.12	7.53 (2, 3, 6)
	6	9.52	
	1	2.90	5.2
	5	6.94	1.0
	4	7.44	2.0
	3	8.63	
	2	9.00	8.5 (2, 3, 6, 8)
	6 (hidden)	-	
	8	9.23	
	7	9.53	3.2
	1	3.06	9.2 (1)
	1	3.42	
	4	6.88	2.0
	2,3	8.70	3.8

TABLE 8

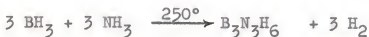
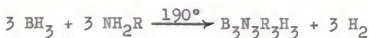
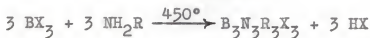
N.M.R. SPECTRAL DATA OF SUBSTITUTED 1-AZA-5-BORABICYCLO [3.3.0] OCTANES

Compound	Peak Assignment	τ	Areas
	1 4,5 2,3,6,8 7	2.56 7.14 8.02 8.86 9.53	4.9 5.2 5.4 7.9 3.0
	1 5 4,5 3 2 6	3.01 7.02 7.89 8.34 9.20 9.68	5.0 .9 6.8 (4, 5,3) 4.3 3.5
	1 4 3 2	3.19 6.76 7.87 8.92	5.0 2.0 2.0 2.2

compound overlapped and could not all be definitely assigned but the total area does agree with the number of hydrogens. The spectrum for the ethyl substituted compound appears to agree on basis of the chemical shifts; however, the total area does not give complete agreement. The boron resonance absorption of 1-n-propyl-5-phenyl-1-aza-5-borabicyclo [3.3.0] octane was found at +8.9 ppm. relative to trimethyl-borate. This chemical shift indicates the presence of the boron-nitrogen bond.⁴⁹

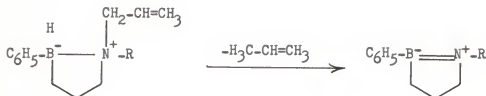
The infrared spectra of the substituted 1-aza-5-borabicyclo [3.3.0] octanes showed the absence of boron-hydrogen and olefinic bonds in the compounds. There were strong absorptions in the 7.8 to 8.0 micron region which were tentatively assigned as due to the boron-nitrogen bond. The boron-nitrogen absorptions of 2'2-iminodiethyl vinyl-benzeneboronates and of pyridine complexes of boranes have been assigned near this region.^{50,51}

The formation of the 1,2-azaborolidines from the reaction of the tertiary diallylamines with triethylamine-phenylborane is rather unique at the temperatures at which the reactions were carried out. Amine-boranes which contain a hydrogen bonded to the nitrogen are known to undergo elimination of that hydrogen with a group bonded to boron, on pyrolysis, to form borazines.⁵² The elimination of



hydrogen from amine-boranes has been accomplished at lower temperatures in solvents.^{52,53} When only one hydrogen is attached to the nitrogen, the reaction stops at conversion to the aminoborane unless drastic pyrolytic conditions are employed.⁵⁴ Amine-boranes which have no hydrogen bonded to the nitrogen have been found to exhibit good stability.⁵⁵ If one of the groups on the boron is an alkyl group, then the compound can disproportionate at high temperatures.⁵⁶

The most likely mechanism for the formation of the 1,2-azaborolidines isolated in this research must involve the formation of a cyclic amine-borane which eliminates the allyl group from the nitrogen. Although no alkene was ever trapped from the reactions, infrared spectra of samples taken during the course of the reaction give some substantiation to this mechanism. The samples were taken while a

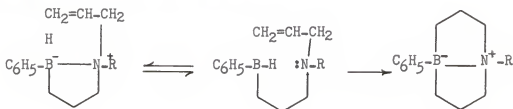


solution of the phenylborane complex and diallyl-n-propyl-amine was being heated to reflux. The boron-hydrogen absorption at 4.3 microns was followed, and it was found that the initial hydroboration occurred between 47 and 60°. The sample at 90° showed little change in intensity from the sample at 73°. However at 112°, before the solution started refluxing, the intensity showed a marked decrease and after refluxing for one and one-half hours, no boron-hydrogen absorption was found. This suggests that the mechanism for loss of boron-hydrogen occurs in two successive steps which is in agreement with the proposed mechanism.

The instability of the cyclic amine-borane toward elimination would be the result of the ease of replacement of the allyl group. The ability of an ethylenic bond of an allylic system to delocalize positive or negative charge over its pi electron system greatly facilitates the reactions of a functional group attached. Quaternary ammonium salts containing allyl groups are known to undergo Hofmann degradation at much lower temperatures and result in better yields than corresponding alkyl ammonium compounds.⁵⁷ Allyl halides undergo S_N2 displacement reactions with ethoxide 37 to 95 times faster than their saturated counterparts.⁵⁸ Not only would the allyl group facilitate the elimination but

the reduction of steric hindrance should also aid. In five-membered rings, the chief source of strain is interaction of non-bonded atoms; removal of the allyl group would reduce the strain.

The bicyclic compounds may be formed by initial intramolecular dihydroborations of the tertiary diallyl-amines before the nitrogen-boron bonds are formed or the bicyclics may result from an equilibrium dissociation of the cyclic amine-boranes followed by hydroboration of the remaining double bond. The position of equilibrium of the reaction would be largely toward the cyclic amine-borane. The stability of the boron-nitrogen bond of the cyclic amine-borane apparently limits the amount of bicyclic compound which can be formed.



1-sec-Butyl-5-phenyl-1-aza-5-borabicyclo [3.3.0] octane was treated under conditions of the synthetic reactions and was found to be completely stable and not a precursor of any other product.

The reaction of triethylamine-phenylborane with diallylphenylphosphine under similar conditions gave

1,5-diphenyl-1-bora-5-phosphabicyclo [3.3.0] octane in 28 per cent yield. No monocyclic product was formed by the reaction and this suggests that the boron-phosphorus bond was not as stable as the boron-nitrogen bond. The dissociation energies for complexes of trimethylamine and trimethylphosphine with trimethylborane, have been found to be 17.6 kcal./mole and 16.5 kcal./mole, respectively.^{59,60}

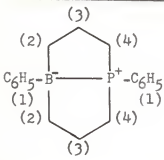
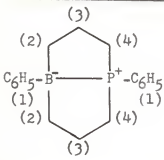
The infrared spectrum of the bicyclic compound showed the absence of boron-hydrogen and olefinic bonds. The nuclear magnetic resonance spectral data are given in Table 9. The spectrum was obtained from a carbon tetrachloride solution of the compound using acetaldehyde as the external standard.

The molecular weight and analysis also agreed with the structure assignment.

Similar reactions were attempted using N,N-di(3-butenyl)aniline, di(3-butenyl)-n-propylamine and allyl-3-butenyl-n-propylamine. The only product which was isolated in these reactions was triphenylborane as the pyridine complex. The reaction of allyl-3-butenyl-n-propylamine was rerun and distillation was attempted in a Hickman still at low pressures. The distillate was a thick viscous liquid which contained no isolatable amount of triphenylborane. The infrared spectrum showed the presence of boron-hydrogen absorption at 4.3 microns and some olefinic bonds.

TABLE 9

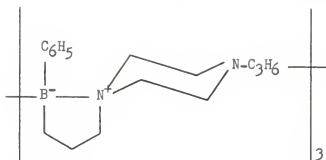
N.M.R. SPECTRAL DATA OF 1,2-DIPHENYL-1-BORA-5-
PHOSPHABICYCLO [3.3.0] OCTANE

Compound	Peak Assignment	τ	Areas
	1	3.13	10.0 (1)
	1	3.23	
	1	3.31	
	4	8.39	12.5 (2, 3,4)
	3	9.04	
	2	9.61	

Unfortunately use of the Hickman still does not result in good separation and no pure products could be isolated. Thus the pot temperatures required for distillation of the products by conventional distilling apparatus are apparently high enough to cause mutual replacement.

The synthesis of 1-phenyl-1-bora-5-azoniaspiro [4.5] decane was repeated using the reaction of triethylamine-phenylborane and *N*-allylpiperidine. The infrared spectrum of this product was identical with the infrared spectrum of the product isolated by the other procedure. The yield was increased to 45 per cent.

An attempt to prepare a polymer containing a cyclic unit was made with the reaction of triethylamine-phenylborane and *N,N'*-diallylpiperazine. Although the stable product was isolated in good yield, the average degree of polymerization was only three. The infrared spectrum of



the product showed an absence of any boron-hydrogen bonds but a small amount of vinyl absorption was present.

The thermal stability of the model compounds prepared in the paper could not be rigorously tested as the differential thermal analyzer was not yet completely assembled. Use of a melting point assembly with the samples in closed capillary tubes did show that the 1,5-diphenyl-1-aza-5-borabicyclo [3.3.0] octane darkened at 270° although the 1-sec-butyl-5-phenyl-1-aza-5-borabicyclo [3.3.0] octane showed no change at 320°. The 1,2-diphenyl-1-bora-5-phosphabicyclo [3.3.0] octane also showed no change at 320°.

The procedure used for the reactions between phenylborane and the unsaturated amines involved placing lithium aluminum hydride with either tetrahydrofuran or diethyl ether in a nitrogen-purged, four-neck, round-bottom flask fitted with a mechanical stirrer, a low temperature thermometer, an addition funnel and a cold-water condenser fitted with a nitrogen inlet tube. The mixture was refluxed for thirty minutes then cooled to -72° with a dry ice-acetone bath. The amine was added in one batch. The diethyl phenylboronate was then added dropwise to the stirring mixture. After complete addition, the mixture was allowed to warm to room temperature. The mixture was filtered in a dry box, then distilled. Further purification depended on the compound synthesized and will be given in the experimental section.

The procedure which was followed to react the triethylamine-phenylborane and the unsaturated amines and

phosphine involved placing the reagents and approximately 2.0 liters of toluene in a one-neck, round-bottom flask with a thermometer well. The flask was then connected to a 60 cm. packed column with a normal fractional distilling head. The solution was slowly heated to reflux and the triethylamine and toluene were slowly distilled. After the pot temperature reached 120°, the remaining small amount of toluene was removed under reduced pressure. The residual liquid was then distilled over a short Vigreux column into several crude fractions. For syntheses giving the 1,2-azaborolidines, the lower boiling fractions were redistilled through a 25 plate spinning band column. The higher boiling fractions were individually dissolved in a small quantity of solvent and cooled to -72° where the solid compounds precipitate. They were then recrystallized. Purification details of the compounds synthesized in this manner are given in the experimental.

All reactions and transfers, except crystallizations, were carried out in a nitrogen atmosphere.

Experimental

Synthesis of 1-phenyl-1-bora-5-azoniaspiro [4.5]-decane from phenylborane and N-allylpiperidine.--Diethyl ether (500 ml.) and 2.5 g. (.06 mole) of lithium aluminum hydride were refluxed then cooled to -72°. The N-allylpiperidine 12.5 g. (.10 mole) was added to the stirring

mixture followed by the dropwise addition of 17.7 g. (.10 mole) of diethyl phenylboronate. After warming to room temperature, the mixture was filtered. The ether was removed and the residual liquid distilled under reduced pressure giving four crude fractions which ranged from 61° (34 mm.) to 160° (.1 mm.). The fraction distilling at 135-145° (.1 mm.) slowly crystallized on setting. The solid was dissolved in light petroleum ether and then cooled to -72° where a white solid precipitated. On filtering, the solid melted, so the petroleum ether was decanted and the remaining removed under reduced pressure. Repetition of the procedure left 3.0 g. (13%) of a white solid, m.p. 34-35.5°.

Anal. Calcd. for $C_{14}H_{22}BN$: C, 78.16; H, 10.31; N, 6.51; B, 5.04. Found: C, 77.98; H, 10.15; N, 6.40; B, 5.17.

Synthesis of 1-phenyl-1-bora-5-azoniaspiro [4.5]-decane from triethylamine-phenylborane and N-allylpiperidine.--

A solution of 1.7 liters of toluene, 19.1 g. (.10 mole) of triethylamine-phenylborane and 12.0 g. (.096 mole) of N-allylpiperidine was distilled at atmospheric pressure until the pot temperature reached 120°. After the remaining toluene was removed, the residual liquid was distilled into three crude fractions. The fractions were dissolved in pentane and cooled to -72°. A white solid precipitated from the fractions distilling at 114-120° and 120-124°

(.03-.05 mm.). The pentane was decanted, the solids combined and the remaining liquid removed under reduced pressure. Repetition of the crystallization gave 9.8 g. (45%) of a white solid, m.p. 34-35°. The infrared spectrum of this compound was identical to that prepared above.

Synthesis of 1-ethyl-2-phenyl-1,2-azaborolidine and 1-ethyl-5-phenyl-1-aza-5-borabicyclo [3.3.0] octane from triethylamine-phenylborane and diallylethylamine.---A solution of 2.0 liters of toluene, 28.8 g. (.15 mole) of triethylamine-phenylborane and 18.8 g. (.15 mole) of diallylethylamine was distilled at atmospheric pressure until the pot temperature reached 120°. After the remaining toluene was removed, the residual liquid was distilled into five crude fractions. The two lowest boiling fractions, 60-92° and 92-107° (.8 mm.), were redistilled through the spinning band column giving 5.9 g. (22.8%) of the clear colorless liquid, 1-ethyl-2-phenyl-1,2-azaborolidine, b.p. 72.5-74.0° (1.3 mm.).

Anal. Calcd. for $C_{11}H_{16}BN$: C, 76.33; H, 9.32; N, 8.09; B, 6.25. Found: C, 76.27; H, 9.23; N, 8.06; B, 6.30.

The remaining three fractions were dissolved in a small amount of acetone and cooled in a dry ice-acetone bath where a white solid precipitated. The solids were filtered, combined and recrystallized from acetone yielding

2.3 g. (7%) of the white solid, 1-ethyl-5-phenyl-1-aza-5-borabicyclo [3.3.0] octane, m.p. 57.5-58.5°.

Anal. Calcd. for $C_{14}H_{22}BN$: C, 78.16; H, 10.31; N, 6.51; B, 5.03. Found: C, 77.87; H, 10.38; N, 6.76; B, 4.87.

Synthesis of 1-ethyl-2-phenyl-1,2-azaborolidine from phenylborane and diallylethylamine.--A solution of 500 ml. of dry tetrahydrofuran and 4.0 g. (.11 mole) of lithium aluminum hydride was refluxed then cooled to -72°. Diallylethylamine (25.0 g., .20 mole) was added to the stirring mixture followed by the dropwise addition of 35.4 g. (.20 mole) of diethyl phenylboronate. After complete addition, the mixture was allowed to warm to room temperature. The mixture was filtered, then the filtrate was distilled at atmospheric pressure removing the tetrahydrofuran. The remaining liquid was distilled through a spinning band column yielding 3.0 g. (8.7%) of a clear colorless liquid, b.p. 68-70° (1.0 mm.). The infrared spectrum of this compound was identical with the 1-ethyl-5-phenyl-1,2-azaborolidine prepared by the other method.

Synthesis of 1-n-propyl-2-phenyl-1,2-azaborolidine and 1-n-propyl-5-phenyl-1-aza-5-borabicyclo [3.3.0] octane from triethylphenylborane and diallyl-n-propylamine.--A solution of 2.0 liters of toluene, 23.0 g. (.12 mole) of

triethylamine-phenylborane and 16.6 g. (.12 mole) of diallyl-n-propylamine was distilled at atmospheric pressure until the pot temperature reached 120°. After the remaining toluene was removed, the residual liquid was distilled into six crude fractions. The lowest boiling fractions, range: 78-83° (1.2 mm.), were redistilled through a spinning band column yielding 7.0 g. (31%) of the clear colorless liquid, 1-n-propyl-5-phenyl-1,2-azaborolidine, b.p. 87.5-90° (2.0 mm.).

Anal. Calcd. for $C_{12}H_{18}BN$: C, 77.04; H, 9.69; N, 7.48; B, 5.78; mol. wt., 187. Found: C, 77.73; H, 9.35; N, 7.40; B, 5.62; mol. wt., 187 (mass spectra).

The three high boiling fractions, ranging from 105° to 165° (1.5 mm.), were dissolved in small amounts of acetone, cooled in a dry ice-acetone bath where a white solid precipitated from each. The solids were filtered, combined and recrystallized from acetone yielding 2.2 g. (8%) of the white solid 1-n-propyl-5-phenyl-1-aza-5-borabicyclo [3.3.0] octane, m.p. 61-62°.

Anal. Calcd. for $C_{15}H_{24}BN$: C, 78.61; H, 10.56; N, 6.11; B, 4.78; mol. wt., 229. Found: C, 78.49; H, 10.66; N, 6.27; B, 4.48; mol. wt., 239 (cryoscopic in cyclohexane).

Synthesis of 1-n-propyl-2-phenyl-1,2-azaborolidine from phenylborane and diallyl-n-propylamine.---A solution of 500 ml. of dry tetrahydrofuran and 3.0 g. (.075 mole) of

lithium aluminum hydride was refluxed then cooled to -72° . The diallyl-n-propylamine (18.8 g., .135 mole) was added to the stirring mixture followed by the dropwise addition of 23.8 g. (.135 mole) of diethyl phenylboronate. After complete addition, the mixture was allowed to warm to room temperature. The mixture was filtered, and the filtrate was distilled at atmospheric pressure to remove the tetrahydrofuran. The residual liquid was then distilled through a spinning band column yielding 3.7 g. (14%) of a clear colorless liquid, b.p. 71° (.3 mm.). The infrared spectrum of this compound was identical to the 1-n-propyl-5-phenyl-1,2-azaborolidine prepared by the other procedures.

Synthesis of 1-n-propyl-2-phenyl-1,2-azaborolidine from triethylamine-phenylborane and allyl-n-propylamine.---A solution of 2.0 liters of toluene, 10.4 g. (.105 mole) of allyl-n-propylamine and 20.0 g. (.105 mole) of triethylamine-phenylborane was distilled at atmospheric pressure. Hydrogen evolution was evident soon after heating of the solution began. After the pot temperature reached 120° , the remaining toluene was removed under reduced pressure. The residual liquid was distilled through a spinning band column yielding 9.2 g. (47%) of a clear colorless liquid, b.p. $78-79^{\circ}$ (.5 mm.). The infrared spectrum of this compound was identical to the 1-n-propyl-2-phenyl-1,2-azaborolidine prepared from diallyl-n-propylamine.

Synthesis of 1-sec-butyl-2-phenyl-1,2-azaborolidine and 1-sec-butyl-5-phenyl-1-aza-5-borabicyclo [3.3.0] octane from triethylamine-phenylborane and sec-butyldiallylamine.--

A solution of 2.0 liters of toluene, 25.6 g. (.167 mole) of sec-butyldiallylamine and 32.0 g. (.167 mole) of triethylamine-phenylborane was distilled at atmospheric pressure until the pot temperature reached 120°. After the remaining toluene was removed, the residual liquid was distilled into three crude fractions. The lowest boiling fraction, 60-110° (.6 mm.), was redistilled over a spinning band column giving 7.1 g. (21%) of the clear colorless liquid, 1-sec-butyl-2-phenyl-1,2-azaborolidine, b.p. 81-82° (.8 mm.).

Anal. Calcd. for $C_{13}H_{20}BN$: C, 77.64; H, 10.02; N, 6.96; B, 5.38; mol. wt., 201. Found: C, 77.61; H, 10.22; N, 7.00; B, 5.76; mol. wt., 201 (mass spectra).

The fraction distilling at 120-130° (.55 mm.) was dissolved in a small amount of acetone and cooled in a dry ice-acetone bath whereupon a solid precipitated. The solid was filtered and recrystallized from acetone yielding 3.8 g. (9.5%) of the white solid, 1-sec-butyl-5-phenyl-1-aza-5-borabicyclo [3.3.0] octane, m.p. 59-60.5°.

Anal. Calcd. for $C_{16}H_{26}BN$: C, 79.03; H, 10.78; N, 5.76; B, 4.45; mol. wt., 243. Found: C, 78.85; H, 10.80; N, 5.74; B, 4.48; mol. wt., 244 (cryoscopic in cyclohexane).

Synthesis of 1,2-diphenyl-1,2-azaborolidine and 1,5-diphenyl-1-aza-5-borabicyclo [3.3.0] octane from triethylamine-phenylborane and N,N-diallylaniline.--A solution of 2.0 liters of toluene, 32.0 g. (.185 mole) of N,N-diallylaniline and 35.2 g. (.185 mole) of triethylamine-phenylborane were distilled at atmospheric pressure until the pot temperature reached 120°. After the remaining toluene was removed, the residual liquid which had a phosphorescent yellow-green color, was distilled into four crude fractions. The two lowest boiling fractions, 70-130° (.5 mm.), were redistilled through a spinning band column yielding 12.2 g. (30%) of the colorless liquid, 1,2-diphenyl-1,2-azaborolidine, b.p. 126-127° (1.1 mm.).

Anal. Calcd. for $C_{15}H_{16}BN$: C, 81.47; H, 7.29; N, 6.34; B, 4.89. Found: C, 81.38; H, 7.42; N, 6.14; B, 5.35.

The highest boiling fractions, 150-160° (.4 mm.), were dissolved in a small amount of acetone and cooled in a dry ice-acetone bath. The solid which precipitated was filtered, then recrystallized twice, from acetone, then pentane to give 11.0 g. (22%) of the white crystalline, 1,5-diphenyl-1-aza-5-borabicyclo [3.3.0] octane, m.p. 80-81°.

Anal. Calcd. for $C_{18}H_{22}BN$: C, 82.13; H, 8.42; N, 5.32; B, 4.11; mol. wt., 263. Found: C, 82.13; H, 8.68; N, 5.48; B, 4.24; mol. wt., 264 (vapor pressure osmometer).

Synthesis of 1,2-diphenyl-1,2-azaborolidine from triethylamine-phenylborane and N-allylaniline.--A solution of 2.0 liters of toluene, 12.7 g. (.095 mole) of N-allylaniline and 20.0 g. (.095 mole) of triethylamine-phenylborane was distilled at atmospheric pressure until the pot temperature had reached 120°. After the remaining toluene was removed, the residual liquid was distilled and a crude fraction 112-118° (.4 mm.) was separated. This fraction was redistilled through a spinning band column yielding 12.3 g. (58%) of a colorless liquid, b.p. 122-123° (.65 mm.). The infrared spectrum of this liquid was identical to the 1,2-diphenyl-1,2-azaborolidine prepared from the N,N-diallylaniline.

Synthesis of 1,5-diphenyl-1-bora-5-phosphabicyclo-[3.3.0] octane.--A solution of 2.0 liters of toluene, 28.6 g. (.15 mole) of diallylphenylphosphine and 28.8 g. (.15 mole) of triethylamine-phenylborane was distilled at atmospheric pressure until the pot temperature reached 120°. After the remaining toluene was removed, the residual liquid was distilled into five crude fractions with a temperature range of 160-260° (.5 to 3.0 mm.). Each fraction was dissolved in a small amount of acetone and cooled in a dry ice-acetone bath. A small amount of solid precipitated from each fraction. The mixtures were filtered, the solids combined and recrystallized twice, from acetone and from diethyl

ether yielding 11.6 g. (28%) of a white solid, m.p. 75.5-76.5°.

Anal. Calcd. for $C_{18}H_{22}BP$: C, 77.16; H, 7.92; P, 11.05; B, 3.86; mol. wt., 280. Found: C, 77.08; H, 7.71; P, 10.90; B, 4.02; mol. wt., 287 (vapor pressure osmometer).

Synthesis of the telomer from triethylamine-phenylborane and N,N'-diallylpiperazine.—A solution of 400 ml. of toluene, 28.8 g. (.15 mole) of triethylamine-phenylborane and 24.9 g. (.15 mole) of N,N'-diallylpiperazine was slowly distilled at atmospheric pressure. After the pot temperature reached 120°, the remaining toluene was removed under reduced pressure with formation of a white solid. The solid was dissolved in benzene and precipitated by pouring the benzene solution into a large volume of pentane. The mixture was filtered and dried yielding 28.8 g. (75%) of a stable white solid which completely melted at temperatures of 200-220°.

Anal. Calcd. for $C_{16}H_{25}BN_2$: C, 75.01; H, 9.83; N, 10.94; B, 4.22. Found: C, 75.11; H, 9.77; N, 10.70; B, 4.27; mol. wt., 660 (vapor pressure osmometer).

Reaction of triethylamine-phenylborane and N,N-di(3-butenyl)aniline.—A solution of 3.0 liters of toluene, 15.9 g. (.083 mole) of triethylamine-phenylborane and 16.8 g. (.083 mole) of N,N-di(3-butenyl)aniline was distilled at atmospheric pressure until the pot temperature reached 120°.

After the remaining toluene was removed, the residual liquid was distilled into six crude fractions, each consisting of a yellow-green liquid with a small amount of white solid. Attempts to precipitate the solid failed. A small amount of solid was isolated by pouring pentane, cooled to -72° , into the mixture and filtering immediately. The solid decomposed slowly in air. The yellow liquid, when in pentane, decomposed almost immediately on contact with air. After setting in the air overnight, the original solid had turned brown. Recrystallization of the brown solid from hexane proved the material remaining was phenylboronic acid, m.p. $210-214^{\circ}$.

Reaction of di(3-butenyl)-n-propylamine and triethylamine-phenylborane.---A solution of 2.0 liters of toluene, 15.2 g. (.08 mole) of triethylamine-phenylborane and 14.2 g. (.085 mole) of di(3-butenyl)-n-propylamine was distilled at atmospheric pressure until the pot temperature reached 120° . After the remaining toluene was removed under reduced pressure, the liquid was distilled into seven crude fractions. Six of the fractions, distilling from $120-195^{\circ}$ (2.0 mm.), contained a light yellow liquid and a white solid. Both decomposed in air, turning dark brown. Attempts at separating the solid from the liquid by precipitation from solution failed. A small amount of the solid was isolated by pouring cold pentane into the mixture and

filtering immediately. The solid was then dissolved in ether and a small quantity of pyridine added. A solid precipitated immediately. The remaining fractions were dissolved in ether and pyridine added. Solids formed immediately. The solids were combined and recrystallized from acetone yielding 1.3 g. of pyridine-triphenylborane, m.p. 212-214° (dec.), lit.⁶¹ 214° (dec.). Under nitrogen the compound melted at 245-247°.

Reaction of triethylamine-phenylborane and allyl-3-butenyl-n-propylamine.--A solution of 2.0 liters of toluene, 11.5 g. (.06 mole) of triethylamine-phenylborane and 9.0 g. (.06 mole) of allyl-3-butenyl-n-propylamine was distilled at atmospheric pressure until the pot temperature reached 120°. After the remaining toluene was removed the residual liquid was distilled into three fractions. The first, 115-150° (1.4 mm.) contained only a few drops of liquid. The two higher boiling fractions, 160-180° (4.0 mm.) and 175-195° (2.0 mm.) contained a white solid and a yellow liquid. Dissolving these in ether and adding pyridine resulted in a solid which on recrystallization from acetone yielded 3.3 g. (51%) of pyridine-triphenylborane, m.p. 245-247° (under nitrogen).

The initial portion of the reaction was repeated. The residual liquid was distilled in a Hickman still at pressures of 10^{-3} to 10^{-4} mm. and the infrared spectrum of

the distillate showed the presence of boron-hydrogen absorption at 4.3 microns and a small amount of vinyl absorption. No single product was isolated by the distillation.

Treatment of 1-sec-butyl-5-phenyl-1-aza-5-borabicyclo-[3.3.0] octane under reaction conditions.--A solution of 100 ml. of toluene and 2.3 g. of 1-sec-butyl-5-phenyl-1-aza-5-borabicyclo [3.3.0] octane was refluxed for thirty-six hours. The toluene was distilled at atmospheric pressure until the pot temperature reached 120°. The remaining toluene was removed under reduced pressure and the residual liquid was distilled giving only one fraction at 120° (.1 mm.). The pot temperatures ranged from 160-230° during the distillation. A small amount of acetone was added to the liquid distillate and the solution was cooled in a dry ice-acetone bath yielding 2.1 g. of white solid, m.p. 58-60°.

Reaction of triethylamine-phenylborane and diallyl-n-propylamine as followed by infrared absorption.--A solution of 2.0 liters of toluene, 28.8 g. (.15 mole) of triethylamine-phenylborane and 20.8 g. (.15 mole) of diallyl-n-propylamine was placed in a three-neck flask fitted with a serum cap and a thermometer. The flask was connected to the distillation apparatus and slowly heated. Samples of 30 ml. were withdrawn at various temperatures

and immediately cooled. The samples were then concentrated to 1 ml. under reduced pressure and the infrared spectra of the sample taken using a cell whose width was .0258 mm. All spectra were obtained using this cell in order to assure uniformity. The intensity of the boron-hydrogen absorption at 4.3 microns was measured from the base line to the peak.

Temperature of solution	Intensity of B-H absorption
24°	55%
47°	49%
60°	35%
73°	25%
90°	22%
112°	8%
112° (after refluxing for 90 minutes)	0%

CHAPTER VI

SUMMARY

Four substituted 1-aza-5-borabicyclo [3.3.0] octanes, a new class of compounds, and four previously unreported 1,2-azaborolidines were prepared and characterized. The compounds were obtained from a novel reaction between triethylamine-phenylborane and tertiary diallylamines. A mechanism for the reaction was proposed, based on qualitative data. Two of the 1,2-azaborolidines were also prepared from the reaction between triethylamine-phenylborane and secondary allylamines.

A new compound, 1-phenyl-1-bora-5-azoniaspiro [4.5]-decane was prepared by the reaction of triethylamine-phenylborane and N-allylpiperidine.

A telomer with an unusual structure was prepared from N,N'-diallylpiperazine and triethylamine-phenylborane.

The compound, 1,5-diphenyl-1-bora-5-phosphabicyclo [3.3.0] octane was prepared and characterized. This compound, representing the first heterobicycloalkane of this type, was synthesized from the reaction of triethylamine-phenylborane and diallylphenylphosphine.

Tetraethyl-p-phenylenediboronate was prepared and characterized.

Several new tertiary unsaturated amines, used as intermediates, were prepared and characterized.

Although rigorous testing of the thermal stability of the bicyclic compounds was not possible, several compounds did show a potential for use in polymers having thermal stability.

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BIOGRAPHICAL SKETCH

Gary Lewis Statton was born on November 4, 1937, in New Brighton, Pennsylvania. He attended public schools in Beaver Falls, Pennsylvania and was graduated from Beaver Falls Senior High School in 1955. He attended Geneva College and was awarded the degree of Bachelor of Science in 1959, graduating with honors.


In September, 1959, he entered the graduate school of the University of Florida and has been in attendance since that date. During this time, he has held the position of graduate assistant and graduate fellow.

The author is a member of the American Chemical Society.

The author is married to the former Shirley Evelyn Walker and is the father of three children.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.


April 18, 1964



Dean, College of Arts and Sciences

Dean, Graduate School

Supervisory Committee:



Chairman

